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$Sc_{44}Os_7$ and $Sc_{44}Ir_7$ with the $Mg_{44}Rh_7$ Structure Type

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Abstract

The $Mg_{44}Rh_7$ structure type with space group $F\bar{4}3m$ and $Z = 8$ is found for $Sc_{44}Os_7$ [$a = 20{\cdot}771\ (5)$ Å, $D_x = 4{\cdot}906\ (4)$ Mg m^{-3}, μ(Mo $K\alpha$) = 27·2 mm^{-1}, $F(000) = 11\,648$] and $Sc_{44}Ir_7$ [$a = 20{\cdot}755\ (3)$ Å, $D_x = 4{\cdot}937\ (2)$ Mg m^{-3}]. $Sc_{44}Os_7$ positional parameters were refined from single-crystal diffractometer data to a final weighted $R = 0{\cdot}052$. $Sc_{44}Ir_7$ with the same structure was obtained by heat treatment at 1023 K. Its isotypy with $Sc_{44}Os_7$ was recognized from powder photographs. The structure can be described by a packing of nested polyhedra units. Their sequence along the cube diagonal is γ-brass, γ-brass*, α-Mn(–C), Ti_2Ni.

Introduction

No phase diagrams of the Sc-rich part of the Sc–Os or Sc–Ir systems are available in the literature. The only known phases are ScIr with the CsCl structure (Aldred, 1962) and $Sc_{11}Os_4$ ($Sc_{11}Ir_4$) recently reported by Chabot, Cenzual & Parthé (1980*a*). The structure of the latter two compounds is face-centred cubic and closely related to the Th_6Mn_{23} type. In the course of these studies the presence of another cubic phase was oberved, of which the identification and structure form the content of this paper.

Experimental

Alloys were prepared by arc-melting techniques, under an argon atmosphere, from elements of high purity (sublimed Sc 99·95% and 99·9% for transition elements of Group VIII).

A single crystal of 50 μm mean diameter was isolated from a crushed ingot with starting composition equivalent to Sc_6Os. The true composition of this phase was revealed later to be $Sc_{44}Os_7$. The structure is cubic, with a cell parameter $a = 20{\cdot}771\ (5)$ Å, obtained from the least-squares refinement of 2θ values of 20 reflexions measured with the lattice-parameter-determination program of a Philips PW 1100 diffractometer. According to the Laue group ($m3m$) and the lack of systematic extinctions other than those due to the F Bravais lattice the possible space groups are $F432$, $F\bar{4}3m$ and $Fm3m$. Data collection was carried out on the automatic four-circle diffractometer in the θ–2θ mode with graphite-monochromated Mo $K\alpha$ radiation, up to $\sin\theta/\lambda = 0{\cdot}61$ Å^{-1}, yielding 402 independent reflexions.

A comparison of a Guinier powder pattern of the Sc_6Os crushed melt with a *LAZY PULVERIX* simulated powder pattern (Yvon, Jeitschko & Parthé, 1977), using the point positions of the $Mg_{44}Rh_7$ structure type* (Westin & Edshammar, 1971), suggested that both compounds are probably isotypic. The refinement of the structure was carried out in space group $F\bar{4}3m$, isotypy with $Mg_{44}Rh_7$ being assumed. Scattering factors and anomalous-disperison corrections were taken from *International Tables for X-ray Crystallography* (1974). Intensities were corrected for spherical absorption and structure factors were corrected for isotropic secondary extinction. The structure refinement using the full-matrix least-squares program *CRYLSQ* (XRAY system, 1976) was obtained from 385 reflexions with $|F| > 3\sigma_F$. In a first

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* This structure type was determined independently by Samson & Hansen (1972) on $Na_{44}Tl_7$. For reasons of simplicity they call their phase Na_6Tl.

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attempt the refinement led to R ($=\sum|\Delta F|/\sum|F_o|$) = 0·085 but the isotropic temperature factor for one atom was negative. Because of the high anomalous-dispersion term of Os, the non-validity of the Friedel law significantly affects the structure factors. By changing the signs of the atomic coordinates the anomaly in the temperature factor vanished and the final R value reduced to 0·073 (R_w = 0·052 with $w = 1/\sigma_F^2$).* The final positional and isotropic thermal parameters are listed in Table 1, interatomic distances in Table 2.

Isotypic compounds and phase transformations

The $Mg_{44}Rh_7$ structure type has also been reported for other Mg–transition-metal alloys like $Mg_{44}Ru_7$ (Westin & Edshammar, 1973) and $Mg_{44}Ir_7$ (Westin & Edshammar, 1972). $Mg_{\sim 6}Pd$ (Samson, 1972) and isotypic $Mg_{\sim 6}Pt$ (Westin, 1972) have a different but closely related cubic structure with 396 instead of 408 atoms in the unit cell. The frequent occurrence of the $Mg_{44}Rh_7$ and $Mg_{\sim 6}Pd$ types with various Mg–transition-metal alloys led us to investigate other Sc–transition-metal alloys for isotypic phases. Sc–T samples in the proportion 6:1, with T = Ru, Rh, Pd, Ir and Pt, were prepared in the same manner as described for $Sc_{44}Os_7$. Examination of the powder patterns of the

Table 1. *The atomic coordinates of* $Sc_{44}Os_7$ *with the* $Mg_{44}Rh_7$ *structure type* (*space group* $F\bar{4}3m$)

The coordinates correspond to the atom closest to the centre of the appropriate nested-polyhedra unit. For the abbreviated polyhedron notation see text. The numbering of the atoms is the same as in the original work on $Mg_{44}Rh_7$. Isotropic temperature factors are expressed as $T = \exp[-2\pi^2 \times 10^{-2}\, U(2\sin\theta/\lambda)^2]$. E.s.d.'s are given in parentheses.

	Unit centre	Polyhedron	Equipoint			x	z	U (Å^2)
A	γ-brass unit	IT	16(*e*)	x,x,x	Sc(11)	0·0570 (6)		0·8 (5)
	0,0,0	OT	16(*e*)	x,x,x	Os(2)	0·9194 (1)		0·9 (1)
		OH	24(*f*)	$x,0,0$	Sc(7)	0·189 (2)		1·0 (4)
		CO	48(*h*)	x,x,z	Sc(5)	0·1610 (5)	0·0209 (7)	1·3 (3)
B	γ-brass* unit	IT	16(*e*)	x,x,x	Sc(8)	0·3087 (7)		0·9 (5)
	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$	OT	16(*e*)	x,x,x	Sc(9)	0·1612 (6)		0·4 (4)
		OH	24(*g*)	$x,\frac{1}{4},\frac{1}{4}$	Os(1)	0·4085 (2)		2·5 (1)
		CO	48(*h*)	x,x,z	Sc(4)	0·4100 (6)	0·2833 (8)	2·3 (4)
C	α-Mn(–C) unit	TT	48(*h*)	x,x,z	Sc(1)	0·5554 (5)	0·6634 (7)	1·5 (3)
	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	T	16(*e*)	x,x,x	Sc(10)	0·4416 (7)		1·6 (6)
		CO	48(*h*)	x,x,z	Sc(3)	0·6978 (5)	0·5158 (7)	1·3 (3)
D	Ti_2Ni unit	T	16(*e*)	x,x,x	Os(3)	0·6503 (2)		1·2 (1)
	$\frac{3}{4},\frac{3}{4},\frac{3}{4}$	OH	24(*g*)	$x,\frac{3}{4},\frac{3}{4}$	Sc(6)	0·8564 (9)		1·1 (4)
		CO	48(*h*)	x,x,z	Sc(2)	0·8931 (4)	0·7857 (7)	1·3 (3)

Table 2. *Interatomic distances* (Å) *in* $Sc_{44}Os_7$ *up to* 4·3 Å

E.s.d.'s are given in parentheses.

(*A*) γ-Brass unit

Sc(11) *A* IT	–3Os(2) *A* OT	2·94 (1)
	–3Sc(5) *A* CO	3·14 (1)
	–3Sc(7) *A* OH	3·21 (2)
	–3Sc(11) *A* IT	3·35 (1)
	–1Sc(9) *B* OT	3·75 (2)
Os(2) *A* OT	–3Sc(2) *D* CO	2·88 (1)
	–3Sc(11) *A* IT	2·941 (2)
	–3Sc(5) *A* CO	3·16 (1)
	–3Sc(7) *A* OH	3·26 (1)
Sc(7) *A* OH	–2Sc(2) *D* CO	3·182 (8)
	–2Sc(11) *A* IT	3·21 (2)
	–2Os(2) *A* OT	3·26 (1)
	–2Sc(4) *B* CO	3·29 (1)
	–4Sc(5) *A* CO	3·42 (1)
	–2Sc(1) *C* TT	3·47 (2)
Sc(5) *A* CO	–1Sc(9) *B* OT	2·91 (1)
	–1Os(1) *B* OH	2·996 (9)
	–2Sc(2) *D* CO	3·08 (1)
	–2Sc(3) *C* CO	3·12 (1)
	–1Sc(11) *A* IT	3·14 (1)
	–1Os(2) *A* OT	3·16 (1)
	–2Sc(4) *B* CO	3·27 (2)
	–2Sc(7) *A* OH	3·42 (1)
	–2Sc(5) *A* CO	4·11 (1)

(*B*) γ-Brass* unit

Sc(8) *B* IT	–3Os(1) *B* OH	2·69 (1)
	–3Sc(4) *B* CO	3·02 (1)
	–3Sc(9) *B* OT	3·18 (1)
	–3Sc(8) *B* IT	3·44 (1)
Sc(9) *B* OT	–3Sc(5) *A* CO	2·91 (1)
	–3Os(1) *B* OH	2·983 (8)
	–3Sc(8) *B* IT	3·18 (1)
	–3Sc(4) *B* CO	3·28 (1)
	–1Sc(11) *A* IT	3·75 (2)
Os(1) *B* OH	–2Sc(8) *B* IT	2·69 (1)
	–2Sc(3) *C* CO	2·70 (1)
	–2Sc(9) *B* OT	2·983 (8)
	–2Sc(5) *A* CO	2·996 (9)
	–4Sc(4) *B* CO	3·39 (1)
Sc(4) *B* CO	–1Sc(8) *B* IT	3·02 (1)
	–2Sc(3) *C* CO	3·16 (1)
	–2Sc(5) *A* CO	3·27 (2)
	–1Sc(9) *B* OT	3·28 (1)
	–2Sc(1) *C* TT	3·29 (1)
	–1Sc(7) *A* OH	3·29 (1)
	–2Os(1) *B* OH	3·39 (1)
	–1Sc(10) *C* T	3·41 (1)
	–2Sc(4) *B* CO	3·72 (1)

(*C*) α-Mn(–C) unit

Sc(10) *C* T	–6Sc(1) *C* TT	3·21 (1)
	–3Sc(4) *B* CO	3·41 (1)
	–3Sc(10) *C* T	3·43 (1)
Sc(1) *C* TT	–1Os(3) *D* T	2·802 (7)
	–1Sc(2) *D* CO	2·95 (1)
	–2Sc(3) *C* CO	3·15 (1)
	–2Sc(1) *C* TT	3·17 (1)
	–2Sc(10) *C* T	3·21 (1)
	–1Sc(1) *C* TT	3·253 (10)
	–2Sc(4) *B* CO	3·29 (1)
	–1Sc(7) *A* OH	3·47 (2)
Sc(3) *C* CO	–1Os(1) *B* OH	2·70 (1)
	–1Sc(6) *D* OH	3·06 (2)
	–1Sc(3) *C* CO	3·06 (1)
	–1Os(3) *D* T	3·12 (1)
	–2Sc(5) *A* CO	3·12 (1)
	–2Sc(1) *C* TT	3·15 (1)
	–2Sc(4) *B* CO	3·16 (1)
	–2Sc(2) *D* CO	3·23 (1)

(*D*) Ti_2Ni unit

Sc(6) *D* OH	–2Os(3) *D* T	2·931 (2)
	–2Sc(3) *D* TT	3·06 (1)
	–4Sc(6) *D* OH	3·12 (2)
	–4Sc(2) *D* CO	3·16 (2)
Os(3) *D* T	–3Sc(1) *C* TT	2·802 (7)
	–3Sc(6) *D* OH	2·931 (2)
	–3Sc(2) *D* CO	3·08 (1)
	–3Sc(3) *C* CO	3·12 (1)
Sc(2) *D* CO	–1Os(2) *A* OT	2·88 (1)
	–1Sc(1) *C* TT	2·95 (1)
	–2Sc(5) *A* CO	3·08 (1)
	–1Os(3) *D* T	3·08 (1)
	–2Sc(2) *D* CO	3·15 (1)
	–2Sc(6) *D* OH	3·15 (1)
	–1Sc(7) *A* OH	3·182 (8)
	–2Sc(3) *C* CO	3·23 (1)

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* A list of structure factors for $Sc_{44}Os_7$ has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35368 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

unannealed samples revealed a body-centred-cubic phase with $a \sim 14$ Å for the Sc–Ru, Sc–Rh, Sc–Ir and Sc–Pt samples [the refined value for the Sc–Rh phase is 14·393 (4) Å]. After annealing at 1023 K under an argon atmosphere for three weeks the patterns of the Sc–Ru, Sc–Rh and Sc–Pt samples remained unchanged; however, the Sc–Ir sample gave a powder pattern corresponding to the $Mg_{44}Rh_7$ structure type. The cell parameter for $Sc_{44}Ir_7$ [a = 20·755 (3) Å] was calculated by least squares from 2θ values measured on a Guinier film obtained with Cu $K\alpha$ radiation and using an internal Si standard.

Discussion

For the $Mg_{44}Rh_7$ structure type three different descriptions can be found in the literature. Westin & Edshammar (1972) describe the structure as built up of a framework of Mg icosahedra, each of which is centred by a Rh atom. The framework of edge- and corner-sharing icosahedra comprises all atoms of the structure except for empty Mg tetrahedra, four per unit cell, which are found in interstices between the icosahedra. Samson & Hansen (1972) in their description of isotypic $Na_{44}Tl_7$ use much larger building blocks. They consider an aggregate consisting of 14 icosahedra and 42 pentagonal prisms, identical to one of the four complexes they had previously found in Cu_4Cd_3. In $Na_{44}Tl_7$ four such aggregates share edges and faces; they account for 392 of the 408 atoms in the unit cell.

The description of Andersson (1978) is the most complete, because it allows the Mg point position to be calculated from an idealized structure model and the cubic unit-cell parameter to be expressed in terms of the Mg–Mg distance. Andersson distinguishes between a framework of Mg octahedra and additional Mg polyhedra groupings positioned in the holes of the framework. The framework is formed with interconnected polyhedra units of two types, one the 'Keggin unit'* (K) consisting of 40 Mg atoms and the other the 'capped pyrochlore unit'† (P) with 18 + 24 = 42 Mg atoms. The two Mg atom groupings within the framework are the *stella quadrangula*‡ (SQ) or 'tetrahedron star' with 8 atoms and a triangle-capped tetrahedron (CT) consisting of 10 Mg atoms. The spatial arrangement of these different groupings is shown in Fig. 1 in a schematic way. We note that the centres of the P and K units are arranged as the Zn and S atoms in zinc blende. The idealized Mg atom point positions given by Andersson were derived by assuming regular octahedra and tetrahedra in the different units. The Rh atoms are then to be found at the centres of the icosahedral interstices.

Our efforts to develop a simplified geometrical description for different cubic 'giant-cell' crystal structures (Chabot, Cenzual & Parthé, 1980*b*) led us to re-examine the structure of $Mg_{44}Rh_7$ according to our own point of view. If the chemical differences between Mg and Rh atoms are disregarded (thus only structure sites are considered) $Mg_{44}Rh_7$ can be imagined as being built up from three types of nested polyhedra units, all having a cubo-octahedron as outermost polyhedron. The nested-polyhedra concept does not permit the point positions to be derived (or at least not with the same precision as is possible with Andersson's model), but offers the advantage of being simple. The nested polyhedra are centred at the highest point symmetries of the structure and each type of polyhedron can be easily recognized by examination of its corresponding equipoint. The three types of nested polyhedra units found in $Mg_{44}Rh_7$ are the 'Ti_2Ni unit' [22 atoms; octahedron (OH) + tetrahedron (T) + cubo-octahedron (CO)], the 'γ-brass unit' [26 atoms; inner tetrahedron (IT) + outer tetrahedron (OT) + octahedron (OH) + cubo-octahedron (CO)] and the non-centred 'α-Mn unit', abbreviated as 'α-Mn(–C)' [28 atoms; tetrahedron (T) + truncated tetrahedron

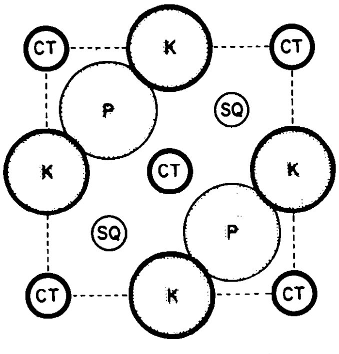

Fig. 1. Schematic drawing of the spatial arrangement of Andersson's Mg polyhedra units in $Mg_{44}Rh_7$. Circles drawn with thin lines are a quarter of a translation period behind those drawn with thick lines. Shaded circles belong to the P and K framework defined by Andersson. Using the F Bravais lattice translation one can generate the complete three-dimensional framework. Each K or P is connected to four P's or K's respectively. K: Keggin's unit with 40 atoms formed by Mg(1), Mg(4), Mg(10) and Mg(3). The latter equipoint is shared with the P unit. P: Capped pyrochlore unit with 42 atoms formed by Mg(2), Mg(5), Mg(6) and Mg(3), the latter being shared with the K unit. SQ: *Stella quadrangula* of 8 atoms formed by Mg(8) and Mg(9). CT: Triangle-capped tetrahedron of 10 atoms formed by Mg(7) and Mg(11).

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* This corresponds to the O atom arrangement in the Keggin polyanion $[PW_{12}O_{40}]^{3-}$ (Keggin, 1934; see also Wells, 1975), a complicated arrangement of twelve edge-shared octahedra.

† The uncapped pyrochlore unit consists of four corner-shared octahedra and corresponds to a fragment of the infinite X anion arrangement in the pyrochlores with general formula $A_2^{[8]}B_2^{[6]}X_6Y$ (see Wells, 1975). Eight face-sharing octahedra are added to form the capped pyrochlore unit.

‡ A five-tetrahedra group to be alternately described as a central tetrahedron with every face capped by an extra atom. The term was coined in analogy to Kepler's *stella octangula*, an octahedron where every face is capped with an extra atom.

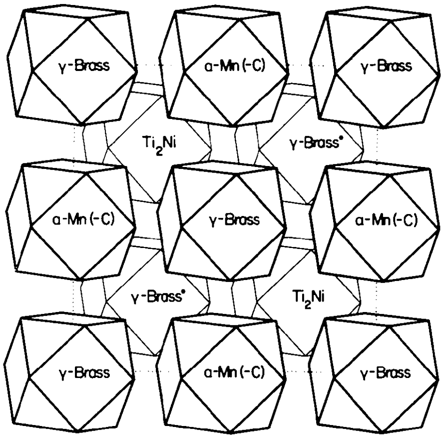

Fig. 2. A section of the unit cell of $Mg_{44}Rh_7$ showing the arrangement of the nested polyhedra units. Partly visible cubo-octahedra correspond to units $\frac{1}{4}$ of a translation period behind.

(TT) + cubo-octahedron (CO)]. To describe the structure in a concise manner it is sufficient to write down the sequence of the nested polyhedra units centred at 000, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$ along the cube diagonal. For the $Mg_{44}Rh_7$ structure type this sequence is: γ-brass, γ-brass*, α-Mn(—C), Ti_2Ni. An asterisk is used to indicate that the second γ-brass unit differs from the first in the atom distribution on the polyhedra sites. The atoms listed in Tables 1 and 2 have been arranged in four groups corresponding to the four nested polyhedra units along the cube diagonal. With the F Bravais lattice translation it follows that $Mg_{44}Rh_7$ contains 16 geometric units per cell, the spatial arrangements of which are shown in Fig. 2. This figure, except for the difference in perspective angle, can be directly compared with Fig. 1.

We have mentioned earlier that Mg_6Pd is very similar to $Mg_{44}Rh_7$. This structure can be described with nested polyhedra units with the characteristic sequence γ-brass, Ti_2Ni, α-Mn, Ti_2Ni along the cube diagonal. It follows that the replacement of the γ-brass* unit by a Ti_2Ni unit is the major difference between the structures. The α-Mn unit differs from the α-Mn(—C) unit by the presence of an atom at its centre.

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